



Physicochemical characterisation of torrefied biomass

Raimie H.H. Ibrahim^a, Leilani I. Darvell^a, Jenny M. Jones^{a,*}, Alan Williams^b

^a Energy Research Institute (ERI), School of Process, Environmental and Materials Engineering (SPEME), University of Leeds, Leeds LS2 9JT, UK

^b Energy Technology and Innovation Institute (ETII), SPEME, University of Leeds, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:

Received 27 June 2012

Accepted 11 October 2012

Available online 18 October 2012

Keywords:

Torrefaction

Biomass

Solid characterisation

Willow

Eucalyptus

ABSTRACT

Torrefaction is a mild pyrolysis treatment under inert atmosphere that has been found to improve the physical and chemical properties of biomass as a fuel. In this study, several wood fuels: willow, eucalyptus, a mixture of hardwoods (oak and birch) and a mixture of softwoods (pine, larch and spruce) were torrefied at 270 and 290 °C with two residence times (30 and 60 min). Physicochemical properties of the torrefied materials, such as grindability, density, hydrophobicity and surface area were investigated. Furthermore, information was also obtained from microscopic and spectrometric studies, namely transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), to gain an insight into any changes in morphology and chemical composition due to the treatments. Temperature plays a major role during torrefaction and choosing an optimum condition is fundamental to attaining a satisfactory energy yield. Results show the lower temperature and shorter residence time was the best treatment to achieve good physical properties with a relatively high energy yield. When treated at these conditions, the softwood mixture had the highest energy (95%), followed by the hardwood mixture (80%), then willow (79%), and finally eucalyptus (75%). Increasing the severity of the torrefaction conditions greatly improved the physical characteristics of the torrefied biomass, in terms of grindability properties and hydrophobicity. While little difference in porosity and surface area were detected by the methods used, the XPS and FTIR studies showed that torrefaction results in a decrease in the R–OH groups and an increase in C=O groups within the fuels. This results in a decrease in the affinity of the fuels to absorb water, and therefore improves their hydrophobicity. For all the fuels, there was a critical temperature for torrefaction, above which abrupt changes in many properties occurred. These include hydrophobicity, energy yield, and grindability. The critical temperatures were fuel dependent and therefore the results indicate that careful optimisation is required for all fuel types to maximise the benefits of torrefaction whilst maintaining a good energy yield.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The mitigation of climate change, together with the gradual decline and insecurity of non-renewable resources, such as coal, oil and gas, have become the main drivers for the urgent need to make a transition to renewable resources for energy in order to attain a sustainable environment [1]. The European communities (EU) proposed a directive in 2008 for the utilisation of such resources [2]. The agreement aims to establish an overall binding target to achieve reductions in EU greenhouse gases (GHG) emissions of 20% by 2020. The UK has signed up to this EU target and committed to produce 15% of its energy from renewable resources by 2020 [2,3]. Thus, there followed the establishment of the latest Renewable Energy Strategy in 2012, where targets are focused on three

energy sectors: electricity, heat and transport [3]. Of all renewable resources, biomass is considered to be the largest that is utilised worldwide, which includes underdeveloped, developing and developed countries [4]. It has a higher availability than most renewables such as wind and hydropower [5]. Moreover, well-managed and regulated biomass is a sustainable source of energy, offering significant life-cycle GHG savings compared to fossil fuels. The carbon dioxide produced from burning biomass is captured during plant growth and thus it is perceived as carbon-neutral and able to reduce the net carbon dioxide emissions when displacing fossil fuel use [6]. However, GHG emissions from cultivation, harvesting, drying, storage, transportation and conversion (for example, pelletisation and co-firing) need careful assessment in any fuel procurement strategy.

Biomass absorbs moisture easily which leads to degradation upon long storage and results in a low heating value. This characteristic, coupled with low energy density, makes it more expensive for transportation [7,8]. Furthermore, biomass is fibrous in nature and

* Corresponding author. Tel.: +44 113 343 2477; fax: +44 113 246 7310.
E-mail address: j.m.jones@leeds.ac.uk (J.M. Jones).

tenacious to grind to desired particle sizes and this requires high energy input. It is difficult to accomplish a perfect combustion, and in entrained fuel boilers or gasifiers, finely powdered biomass is required. Therefore, the making of wood pellets is becoming necessary especially in the co-firing industry, where biomass is used with coal in large scale boilers [9]. However, the grinding of wood to pellets is very costly and usually requires high capital investment and maintenance [10]. Prior to grinding, the biomass requires drying as moisture is an important factor during milling. Mani et al. [11] stated that “the higher the moisture content, the higher the specific energy consumption is needed to mill such biomass”.

The chemical and physical properties of a biomass can be upgraded by implementing torrefaction. Torrefaction is a developing area that is believed to become a leading technology [12]. It is a mild pyrolysis pre-treatment, which involves a moderate temperature of above 200 °C in the absence of oxygen. Several studies have been conducted using different temperatures within the range of 200–300 °C and residence times, mainly 30–60 min [4,13–18]. A few studies extended the reaction time to three to five hours [9,19]. In general, all results showed that the more severe the torrefaction conditions are, the easier is the grinding and the greater the amount of energy that can be saved during this process [20]. However, the mass loss of the solid torrefied product must be kept as low as possible to attain a high energy yield [20]. Therefore, choosing an optimum operating condition is crucial, as different types of biomass give different outcomes. What is required and acceptable is that this approach is able to retain approximately 70% of the initial biomass dry weight, and about 80–90% of the biomass's original energy content [7]. Biomass has a higher O/C ratio than coal, which explains its lower calorific value. Torrefaction has the ability to increase this value. Furthermore, this thermal pre-treatment produces a more hydrophobic and grindable solid product compared to the raw material.

In torrefaction, hemicellulose, as one of the main components that make up biomass, is considered to be the most reactive [7,17]. Chen et al. carried out torrefaction processes that focussed on the three lignocellulosic materials using a thermogravimetry and recorded the weight losses with increasing temperature [4]. The results showed that hemicellulose degraded effectively by torrefaction even at a temperature as low as 230 °C [4]. This can be explained by the decomposition of various saccharides and branches in the hemicellulose, which are easy to remove from the main backbone [24]. This effect is followed by the decomposition of cellulose which can eventually take place at higher temperatures [4]. Cellulose is made up of a polymer of glucose with no branches, hence, it is thermally more stable [24]. Lignin does not seem to show any significant impact on torrefaction [4]. It decomposes to three products: a char solid, tars and volatiles/gases, the latter two contributing to the significant loss of mass upon torrefaction at higher temperatures.

With regard to the solid torrefied biomass, there has been a great deal of research considering the standard fuel analysis, mass yield and energy yield [4,13,17,19,21–23]. A few studies report on the improvement of their grindability properties [4,9]. However, very little research has given a thorough look into the structure and physicochemical properties of the solid product [4]. The present study focuses on the investigation of not only the morphology and composition of the solid torrefied biomass (several woody biomass including eucalyptus and short rotation willow coppice (SRC)) but also, on their physical and chemical characteristics. A range of characterisation methods are used, including: transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for morphology examination, X-ray photoelectron spectroscopy (XPS), which is used to study the changes in the O/C ratio and components in the biomass, and Fourier transform infrared spectroscopy (FTIR), to follow changes in chemical structure. The surface

Table 1

Treatment conditions used for the torrefaction experiments.

Treatment	Temperature/°C	Residence time/min
A	270	30
B	270	60
C	290	30

area and pore size distribution are also investigated using the Brunauer–Emmett–Teller (BET) method. Furthermore, the density, hydrophobicity and grindability of the torrefied products are also studied.

2. Experimental

2.1. Samples

The fuels studied were willow, eucalyptus, a mixture of hardwoods (oak and birch) and a mixture of softwoods (spruce, pine and larch). The samples were sourced from farms around Yorkshire in the form of chips in the size range of 10–50 mm.

2.2. Torrefaction process

The samples were treated in a torrefaction rig, which has been described in more detail in Bridgeman et al. [14]. An approximate mass of 100 g of biomass was used per batch and nitrogen and a flow rate of 1.2 mL min^{−1} was supplied to the reactor to ensure an inert atmosphere. The samples were dried at 150 °C for 60 min, followed by further heating at a rate of 10 °C min^{−1} to the final temperature. The final temperatures and residence times used are listed in Table 1. Here, the residence time is taken as the time at which the treatment dwells at the maximum reaction temperature, after which the samples were rapidly quenched under nitrogen flow to prevent further reaction. However, it was noted that the cooling stage exhibited a sample dependency, and cooling to below 200 °C could be of significant duration. Therefore, strictly speaking the residence times were between 10 and 20 min longer than intended (reported). The final temperature in the centre of the bed was also noted to be higher than the set point (up to 20 °C higher), indicating that the torrefaction process can be exothermic. The resulted torrefied product was weighed and the mass yield, η_m was calculated as percentage of the original dry mass sample, as follows

$$\eta_m = \left(\frac{m_{\text{treated}}}{m_{\text{raw}}} \right) \times 100 \quad (1)$$

where m_{treated} is the mass of the torrefied product and m_{raw} is the dry mass of the untreated biomass (both on a dry basis) [14].

2.3. Fuel characterisation

The untreated and torrefied fuels were analysed for ash, moisture, and volatile matter in duplicates, following the methods laid out in standards: CEN/TS 14774:2004 [25], CEN/TS 14775-2:2004 [26] and CEN/TS 15148:2005 [27] respectively. The elemental composition, C, H and N contents were measured, also in duplicates using a CE Instruments Flash EA 1112 Series elemental analyser. The calorific value is calculated from their C, H and N contents in a dry basis, using formula (2), which was derived by Friedl et al. [28]:

$$\text{HHV} = 3.55\text{C}^2 - 232\text{C} - 2230\text{H} + 51.2\text{C} \times \text{H} + 131\text{N} + 20,600 \quad (2)$$

From these calculated calorific values and mass yields, energy yields, η_E , can be determined as follows,

$$\eta_E = \eta_m \times \left(\frac{\text{HHV}_{\text{treated}}}{\text{HHV}_{\text{raw}}} \right) \quad (3)$$

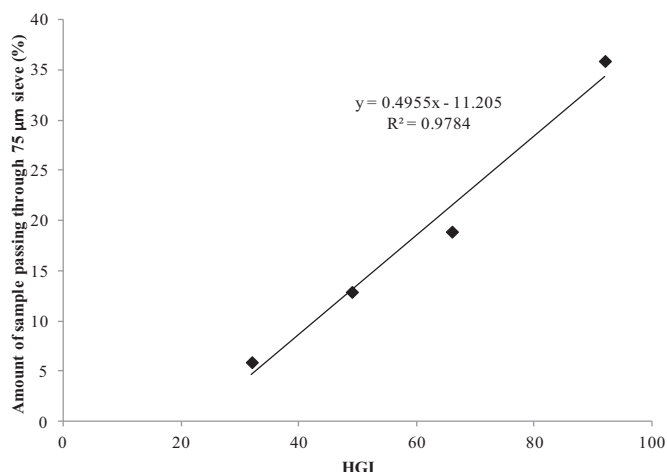


Fig. 1. Calibration curve of Retsch PM100 mill (500 mL) using four standard coals of known HGI values of 32, 49, 66 and 92.

where $\text{HHV}_{\text{treated}}$ is the higher heating value of the torrefied biomass and HHV_{raw} is the higher heating value of the raw biomass, both on a dry basis [13].

2.4. Physical characterisation

2.4.1. Hydrophobicity

To compare the hydrophobicity of the fuels, approximately 0.5 g of biomass (particle size < 1 mm) were immersed in deionised water at room temperature in a sintered glass filter for two hours, followed by air drying for an hour, prior to the determination of its moisture content.

2.4.2. Grindability test

To compare the grindability properties of the fuels, a modified version of the Hardgrove Grindability Index (HGI) was used, as detailed in Bridgeman et al. [14]. In this approach, the same fixed volume (50 cm³) for each coal and biomass samples was used [29,30] instead of a fixed weight. Additionally, a bigger mill size (500 mL) was used than the one originally stated in the method (i.e. 250 mL). For this purpose, a Retsch PM 100 ball mill was calibrated with coals of known HGI values (32, 49, 66 and 92), as described in Bridgeman et al. [14]. Fig. 1 shows the plot of the percentage of sample that passed through a 75 µm sieve against the HGI values for the four coals used to calibrate the 500 mL ball mill. The linear fit was then used to determine the equivalent HGI of the biomass tested as shown in Eq. (4).

$$\text{HGI}_{\text{equiv}} = \frac{m + 11.205}{0.4955} \quad (4)$$

where m is the percentage mass of sample that passed through the 75 µm sieve.

The particle size distribution profiles for the raw and torrefied fuels in comparison to coals were also assessed to give a greater insight into their grindability behaviour, using the method described in Bridgeman et al. [14]. Briefly, the samples were ground using the Retsch SM 100 and a 4 mm screen and then sieved using a series of 1.18 mm and 600 µm sieves. A volume of 50 cm³ of the sample collected on the 600 µm sieve was measured using a measuring cylinder and transferred to the mill to undergo further grinding in a Retsch PM 100 ball mill. The ground sample was then sieved using a series of sieves of mesh sizes 600, 355, 212, 150, 75 and 53 µm. The mass of sample collected on each sieve was measured and recorded as a percentage of the original mass sample.

2.5. Morphology and chemical composition

The BET method was used to determine the surface areas using the Quantachrome Instruments NOVA 2200 Multi-station Any-gas Sorption Analyser Standard Model v10.03. SEM analysis was also carried out to study the changes in structure of the samples due to the treatments. Furthermore, the porosity of torrefied samples was investigated using a Philips F20 Tecnai TEM analyser. Measurements to determine the density of the biomass samples were attempted using the water displacement method in accordance to the wood density protocol by Osazuwa-Peters and Zanne [31]. Rodrigues and Rousset [16] did not observed any significant changes to the bulk density of samples torrefied at low temperature (220 °C), but as the process temperature increased, a decrease in density was observed primarily due to loss of mass. However, in the present work, this technique was not sensitive enough to detect changes in density on the samples studied. The dry masses and volumes recorded in this experiment yielded densities of approximately 1 g cm⁻³ for all the samples tested.

Transmission FTIR was conducted to study the changes in the functional groups of the fuels using a Thermo Scientific Nicolet iS10 FT-IR Spectrometer, and data was collected using the OMNIC software. Prior to this analysis, samples were prepared in KBr wafers, by compressing 3 mg of dried sample with KBr (300 mg). A Thermo Scientific ESCALAB 250 X-ray Photoelectron Spectrometer and CasaXPS software were used to probe the surface chemistry of the thermal treated woods to detect any changes in the components of the torrefied biomass.

3. Results and discussion

3.1. Fuel characterisation and torrefaction conditions

The resultant mass yield for the different samples and torrefaction conditions are listed in Table 2. Table 2 also shows the change in mass yield due to a change in both process temperature and residence time. The results show that temperature plays the most important role in torrefaction. I.e., the final temperature has a greater impact on the change in mass yield than residence time, and this effect is more apparent in willow and softwood (~10% mass loss extra). The greater effect of process temperature over residence time on mass yields has previously been observed by Bridgeman et al. [14], who investigated process variables with a factorial method using a three-factor methodology (temperature, residence time and particle size). They concluded that temperature had the greatest influence on the change in mass yield of willow and Miscanthus, followed by residence time and particle size. However, it can also be observed that, at least in this instance, the hardwoods mixture was slightly more affected by the increase in residence time (−9.87%) than by the increase in temperature (−6.33%). Table 3 presents the influence of different torrefaction conditions on the proximate analysis of the biomass samples in comparison to when they are untreated. It can be seen that air-dried pre-treated fuels have lower moisture contents than the air-dried untreated fuels. Water is the major product of torrefaction [13,17,18]. The loss of water takes place in two mechanisms: during the drying period, prior to torrefaction, and during dehydration reactions between organic constituents upon torrefaction [13]. Table 3 also shows the general trend of decreasing volatile matter and increasing fixed carbon content as the torrefaction conditions become more severe. The ash content also increases, which is related to the loss of mass of organic matter during torrefaction [15]. Table 4 demonstrates the alterations in the chemical composition of the torrefied biomass. As expected, there is an increasing trend in the carbon content, whilst the oxygen and hydrogen contents decrease. The reduction

Table 2
Mass yield of torrefied biomass (dry basis).

Sample	Mass yield (% dry)			Change of mass yield between torrefied biomass (A and B) due to a change in residence time ^a	Change of mass yield between torrefied biomass (A and C) due to a change in temperature ^b
	A	B	C		
Willow	68.76	67.53	56.21	1.23	12.55
Eucalyptus	67.62	56.66	50.61	10.96	17.01
Hardwood	73.00	71.60	59.15	1.40	13.85
Softwood	79.53	74.61	66.50	4.92	13.03

^a Difference between yield for sample A ($t = 30$ min) and sample B ($t = 60$ min), both torrefied at $T = 270$ °C.

^b Difference between yield for sample B ($T = 270$ °C) and sample C (290 °C), both with a residence time of 30 min.

Table 3
Proximate analysis of raw and torrefied biomass samples.

Sample	Moisture (% ar)	Volatile (% daf)	Ash (% dry)	Fixed carbon (% daf)
Raw Willow	6.0	84.8	0.5	15.2
Willow A	3.9	73.8	0.5	26.2
Willow B	3.8	72.4	0.7	27.6
Willow C	3.6	63.2	1.1	36.8
Raw eucalyptus	8.0	80.4	1.6	19.6
Eucalyptus A	4.3	67.9	1.6	32.1
Eucalyptus B	4.3	71.2	2.0	28.8
Eucalyptus C	4.2	60.3	2.2	39.7
Raw hardwood	6.7	83.2	0.7	16.9
Hardwood A	5.0	72.2	1.0	27.8
Hardwood B	3.8	72.0	1.6	28.0
Hardwood C	3.7	64.6	2.1	35.4
Raw softwood	7.0	83.0	0.1	17.0
Softwood A	4.7	79.7	0.1	20.3
Softwood B	4.0	78.3	0.3	21.7
Softwood C	3.9	71.8	0.4	28.2

in the hydroxyl groups with water vapour formation and evolution can explain the significant losses. A consequence of the changing CHO content is the increase in higher heating values. The sulphur contents were below the detection limit, and nitrogen close to the detection limits, hence, no significant changes can be reported. Further illustration of the changes in the chemical composition of torrefied biomass can be observed on the Van Krevelen diagram, shown in Fig. 2. Also shown in Fig. 2 are typical data points for lignite and anthracite. The figure shows the changes result in fuels moving along the coalification series towards the composition of lignite.

Table 4
Ultimate analysis of raw and torrefied biomass samples (daf basis).

Sample	C (%)	H (%)	N (%)	O ^a (%)	HHV (MJ kg ⁻¹)
Raw Willow	49.5	6.1	0.2	44.4	19.4
Willow A	55.6	6.0	0.0	38.4	22.2
Willow B	56.9	5.9	0.0	37.3	22.8
Willow C	60.1	5.8	0.0	34.2	24.2
Raw eucalyptus	49.3	6.5	0.0	44.3	20.5
Eucalyptus A	57.8	6.0	0.0	36.2	22.8
Eucalyptus B	61.9	5.8	0.0	32.3	24.3
Eucalyptus C	69.4	5.3	0.0	25.1	27.3
Raw hardwood	46.8	5.9	0.1	47.2	18.3
Hardwood A	57.7	6.1	0.0	36.2	23.2
Hardwood B	58.4	5.7	0.0	35.8	23.0
Hardwood C	61.4	5.7	0.0	32.9	24.3
Raw softwood	46.7	5.9	0.0	47.4	18.4
Softwood A	54.6	6.3	0.0	39.1	22.1
Softwood B	55.7	6.1	0.0	38.2	22.4
Softwood C	58.7	6.0	0.0	35.3	23.7

^a Calculated by difference. S was not detected.

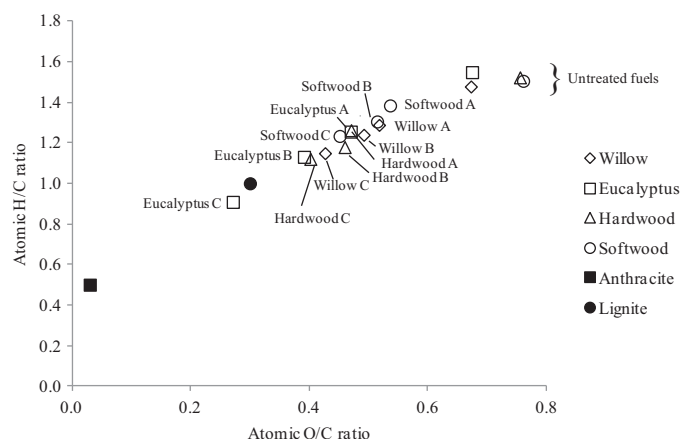


Fig. 2. Van Krevelen plot of raw and torrefied biomass alongside anthracite and lignite.

This change is particularly noticeable for the hardwood samples, including eucalyptus and willow. Fig. 3 shows the relationship between mass yield and energy yield. Of the fuels and conditions studied, all of the torrefied softwood samples have attractive mass and energy yields. The other fuels produced at condition C have mass and energy yields that would be unattractive for a commercial process. Eucalyptus is the most reactive fuel, and as such, only that produced at condition A has a respectable mass and energy yield. It is interesting that the different woody biomass appear to produce a single relationship between mass yield and energy yield, and this implies that optimisation for new woody biomass may be easier than originally anticipated.

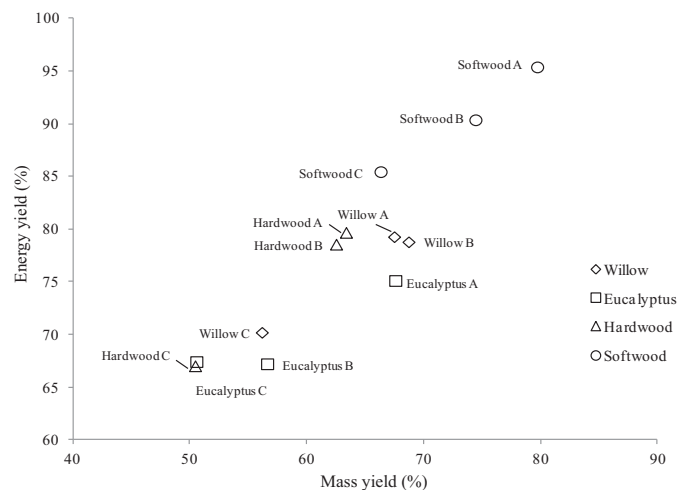


Fig. 3. Energy yield against mass yield for all torrefied biomass (dry basis).

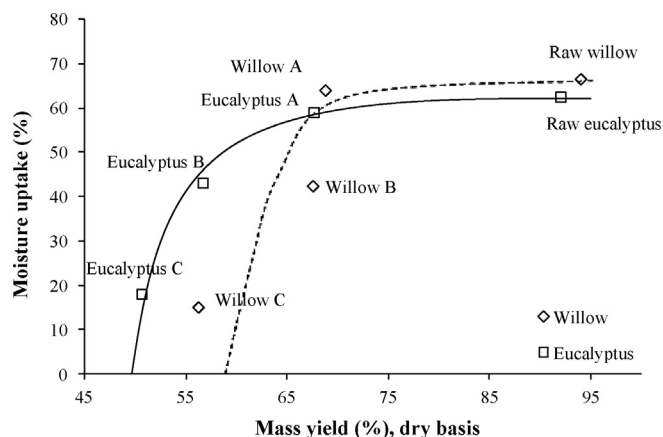


Fig. 4. Variation in moisture uptake (as measured by the water immersion test) with the mass yield of the raw and torrefied willow and eucalyptus samples (treatments A, B, and C).

3.2. Physical characterisation

3.2.1. Hydrophobicity

A plot showing the relationship between the resultant mass yield after the different torrefaction experimental conditions and the moisture uptake of the samples, as measured after the water immersion test, is shown in Fig. 4. There is a general trend for the reduction of absorbed moisture content with mass yield as the torrefaction temperature and residence time increases. Fig. 4 shows that both raw willow and eucalyptus experienced the greatest uptake of water during the two-hours of immersion (66.7% and 62.6% respectively), while willow C and eucalyptus C absorbed the least amount (15.1% and 18.1% respectively). From these findings, torrefaction is proven to improve the physical property of a biomass by increasing its hydrophobicity. This is in agreement with Pimchuai et al. [22] where the hydrophobicity of agricultural residues (such as rice husks) torrefied at different temperatures (250, 270, 300 °C) was investigated and a decrease in absorbed moisture was observed as the torrefaction temperature increased (4.0, 2.6, 2.3% respectively), and when compared to the raw rice husks (36.9%). From these results, it is apparent that the more severe torrefaction conditions yield a drier solid, which is less hydrophilic. Although both properties are desirable in a fuel (hydrophobicity and low moisture content), the process conditions required to achieve these favourable changes can also have a detrimental effect on the energy yields. Fig. 5(a) illustrates the relationship between the energy yield and moisture uptake of torrefied biomass, while Fig. 5(b) correlates moisture uptake with the heating value of the fuel. From Fig. 5(a) and (b), it is clear that the higher process temperature (i.e. treatment C) yields a drier fuel (15–18% moisture) with higher hydrophobicity, and also with the highest heating value (Fig. 5(b)), however this treatment also results in the lowest energy yields (70.2% for willow and 67.4% for eucalyptus). These results highlight the need for optimisation of the torrefaction conditions used in order to improve fuel quality without sacrificing energy yields. From Figs. 4 and 5(b) it is clear that at some point in the torrefaction process there is an abrupt change in the characteristics of the solid product. For both fuels this change happens below ~68% mass yield. For lower mass yields than this, the HHV of the solid and the hydrophobicity increase very sharply.

3.2.2. Grindability of torrefied biomass

Table 5 presents the HGI_{equiv} values of the tested biomass that were determined using the calibration curve shown in Fig. 1. All the raw biomass samples resulted in a HGI_{equiv} of <32 indicating their poor grindability behaviour. The low friability properties of

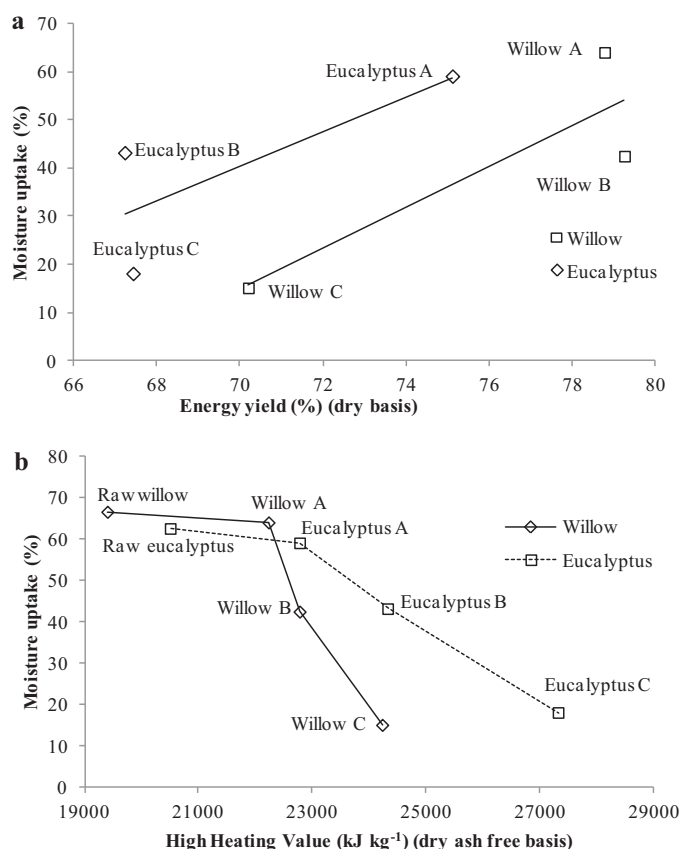


Fig. 5. Relationship between moisture uptake (as measured by the immersion test) and (a) energy yield; (b) high heating value; of raw and torrefied willow and eucalyptus (treatments A, B and C).

the untreated biomass samples are more clearly illustrated in Fig. 6, which shows the particle size distribution curves of the raw samples compared with four standard coals of known HGI values. It can be observed that the HGI_{equiv} values of treated biomass improved with the severity of the torrefaction conditions (see Table 5). As the process conditions became more severe, the torrefied biomass became more grindable or brittle, resulting in a higher fraction of the sample passing through the 75 μ m sieve. Table 5 also shows that compared to the other samples, the hardwood mixture sample was in general less affected by the increasingly aggressive torrefaction treatments.

Fig. 7 shows the plot of the particle size distribution for the raw eucalyptus sample and its torrefied counterparts after milling. The particle size distribution curves of the four reference coals are also shown in Fig. 7, for comparison purposes. It can be noted that there is a marked improvement on the grindability behaviour of the eucalyptus samples when torrefied at increasingly more severe conditions – with Eucalyptus C showing comparable behaviour to coals of HGI 49. This trend was also observed in the other samples. Fig. 8 probes the correlations of the HGI_{equiv} values and (a) the carbon content, (b) the mass yield and (c) the energy yield. It is noted that HGI_{equiv} value increases with increasing carbon content, while it decreases with increasing mass yield and energy yield. There seems to be an abrupt change in the slopes for the plots in Fig. 8, where the HGI_{equiv} value increase significantly when the torrefaction temperature is above a critical value. The point at which the change in slope happens is different for the different fuels. For these fuels the change in slopes are at approximately 55–60% C in the solid, but this condition is met over a wide range of mass yields, from 75% for softwoods to 55% for eucalyptus. This illustrates how sensitive the biomass is to changes in temperature. At the higher

Table 5
Calculated HGI_{equiv} values of raw and torrefied biomass samples.

Sample	m (%)	HGI _{equiv} value	Sample	m (%)	HGI _{equiv} value
Raw willow	0.2	<32	Raw softwood	0.0	<32
Willow A	10.5	64.6	Softwood A	7.7	41.5
Willow C	28.1	86.4	Softwood B	9.9	46.4
			Softwood C	20.3	69.2
Raw eucalyptus	1.7	<32	Raw hardwood	0.3	<32
Eucalyptus A	6.5	38.9	Hardwood A	8.5	43.3
Eucalyptus B	10.1	46.8	Hardwood B	7.8	41.8
Eucalyptus C	25.0	79.6	Hardwood C	17.6	63.3

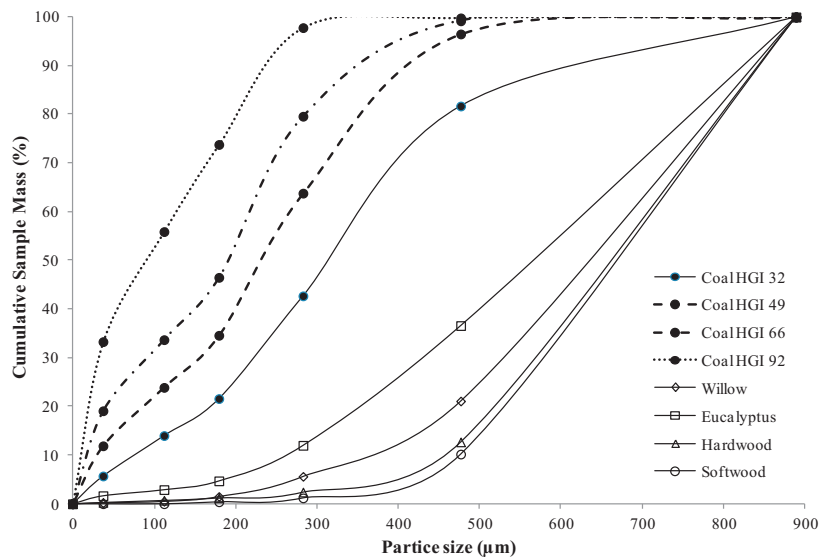


Fig. 6. Cumulative particle size distributions resulting from milling tests of the raw biomass samples compared with standard reference coals of HGI 32, 49, 66 and 92.

temperatures, the hemicellulose decomposition will become very extensive, and in the case of treatment C, the decomposition of cellulose will become appreciable. Cellulose decomposition has been studied extensively. FTIR studies indicate a rapid change in the chemical functional groups once the temperature nears 300 °C [32,33]. At this point OH groups are eliminated rapidly due to dehydration and cross-linking reactions, and C=O groups are created. Coupling of these two factors will mean that the fibres will

become more easy to separate (through degradation of hemicellulose) and the solid will become more hydrophobic. The large mass loss observed for treatment C is further evidence that cellulose decomposition has become very important.

3.3. Morphological changes to the structure of solid torrefied biomass

3.3.1. Surface area

The surface areas of investigated samples using the BET method did not indicate any significant pore development upon torrefaction, as shown in Table 6 for the willow and eucalyptus fuels. Surface areas fall within the range 1.1–3.8 m² g^{−1} and duplicate measurements on some fuels indicate a relative error of approximately 10% of the measurement.

Table 6
BET total surface areas of raw and torrefied biomass samples (size fraction of <0.25 mm).

Sample	Surface area (m ² g ^{−1})
Raw willow	3.8 ± 0.4
Willow A	3.4
Willow B	3.1 ± 0.6
Willow C	1.9
Raw eucalyptus	1.1 ± 0.1
Eucalyptus A	ND
Eucalyptus B	2.7
Eucalyptus C	ND

ND, not determined.

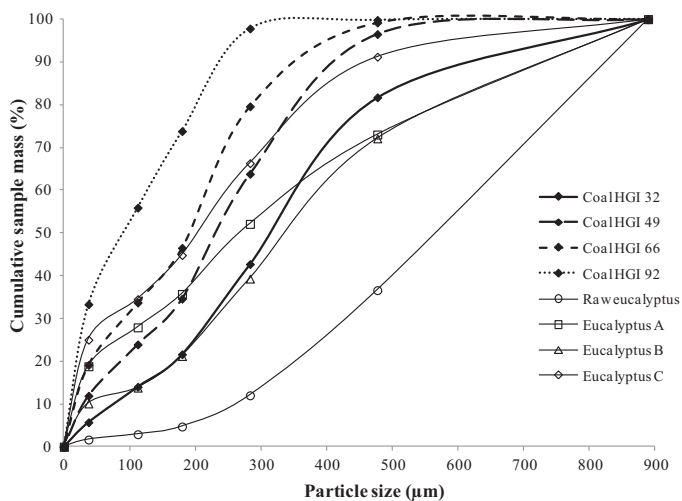


Fig. 7. Cumulative particle size distributions resulting from milling tests of the raw eucalyptus under conditions A, B and C (refer to Table 1), and compared with standard reference coals of HGI 32, 49, 66 and 92.

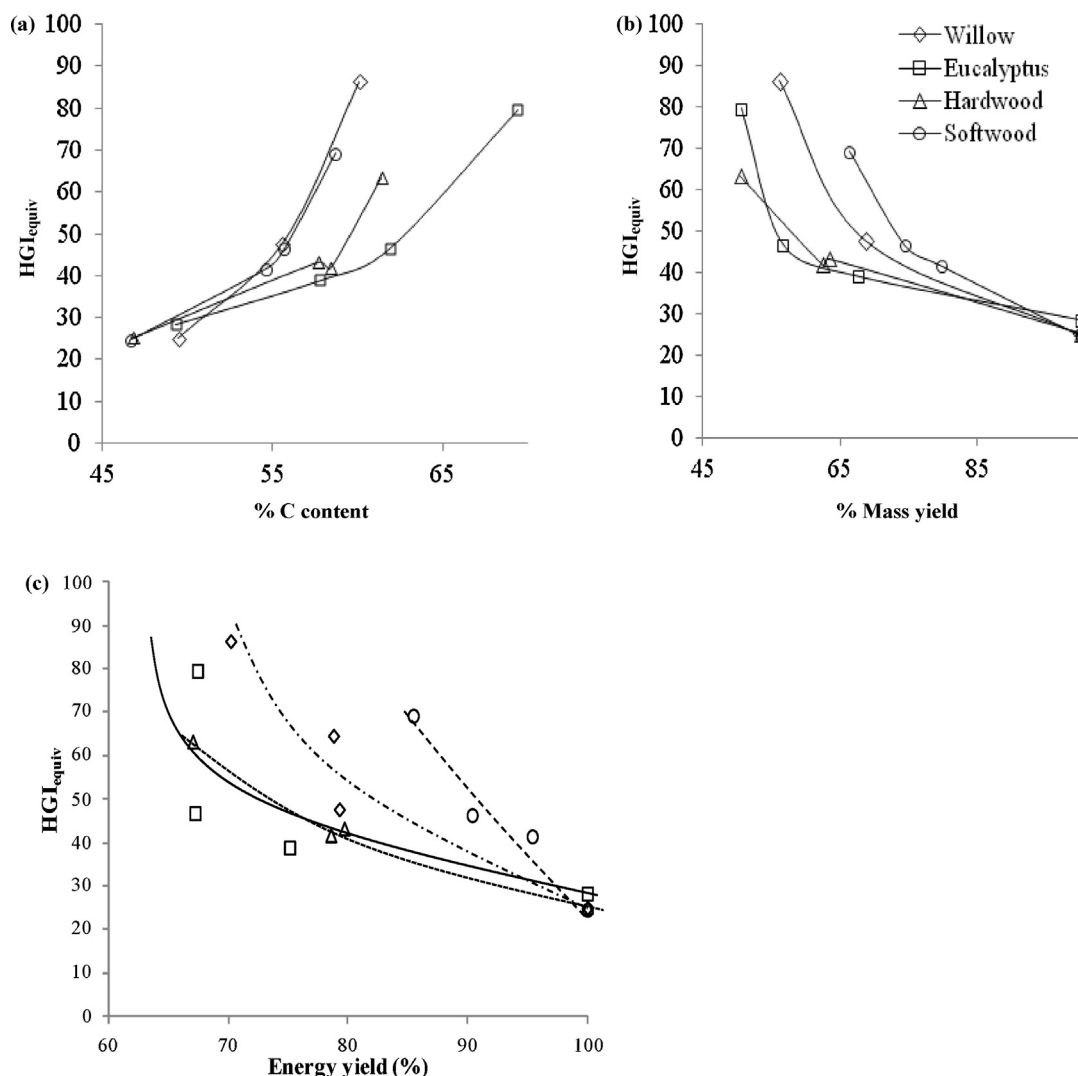


Fig. 8. Relationships of HGI_{equiv} against the (a) C content (dry ash free basis), (b) mass yield (dry basis) and (c) energy yield (dry basis) of raw and torrefied biomass fuels.

3.3.2. Electron microscopy

Fig. 9 shows the SEM images of raw and torrefied willow and eucalyptus at increasing treatment temperatures. It can be seen that the raw biomass contains very strong, bulky xylem tissues. Upon torrefaction, the biomass began to lose its bound fibrous structure, and cracks and fissures became more obvious in the particles. This is particularly evident in the samples torrefied at 290 °C.

3.4. Chemical properties of solid torrefied biomass

3.4.1. FTIR analysis

Fourier transform infrared spectroscopy was used to investigate changes in the chemical structure of the solid torrefied biomass as shown in Fig. 10. These changes are largely due to the degradation of hemicellulose in the biomass. Functional groups of interest are those in the regions where most of the transformation can be observed such as in the O–H, C=O, C=C, C–H and C–O–C groups. In general, the most severely treated biomass has its functional group vibrations shifted towards lower wavenumbers and changes in the intensity can be observed. Rousset et al. [23] observed that the two major bands that shifted are due to vibrations in the C=O and C–O–C groups. Moreover, the shift in wavenumber can also be observed in the C=C group vibrations. In this study, similar changes are observed. Fig. 10 demonstrates the

decrease in intensity of the O–H band around 3600–3100 cm^{−1}, which is more obvious between the raw eucalyptus and eucalyptus C, as well as those for the analogous willow samples. The loss of O–H group explains the improved hydrophobicity of torrefied biomass, and similar decreases in intensity of the OH vibration have been reported previously for torrefied bamboo [23]. Bands at about 1740–1710 cm^{−1} are related to the stretching vibrations of the C=O groups. In raw eucalyptus, the vibration is largely due to the carboxylic acids in hemicelluloses, which can include xyloglucan, arabinoglucuronoxylan and galactoglucomannan, as discussed by Van der Stelt et al. [19]. Previous work suggests that torrefaction eliminates this signal, by decreasing the amount of carboxylic acids groups and leading to new products, which appear at lower wavenumbers (1700 cm^{−1}) [34]. Upon torrefaction, the C=C stretch moves to lower wavenumber and, in the case of the eucalyptus samples, also increases in intensity. The degradation of hemicelluloses can result in an increase in unsaturation, which can explain the observed trends; that is, there is formation of more non-polar and unsaturated compounds in the torrefied samples. The C–O–C vibrations in cellulose appear in the 1250–1220 cm^{−1} region, and the intensity of bands in this region tends to decrease for the torrefied samples. Also, the decrease in the intensity of this band is more extensive as the severity of torrefaction conditions increases. With regards to lignin, the vibrations at 1269 cm^{−1} could be due

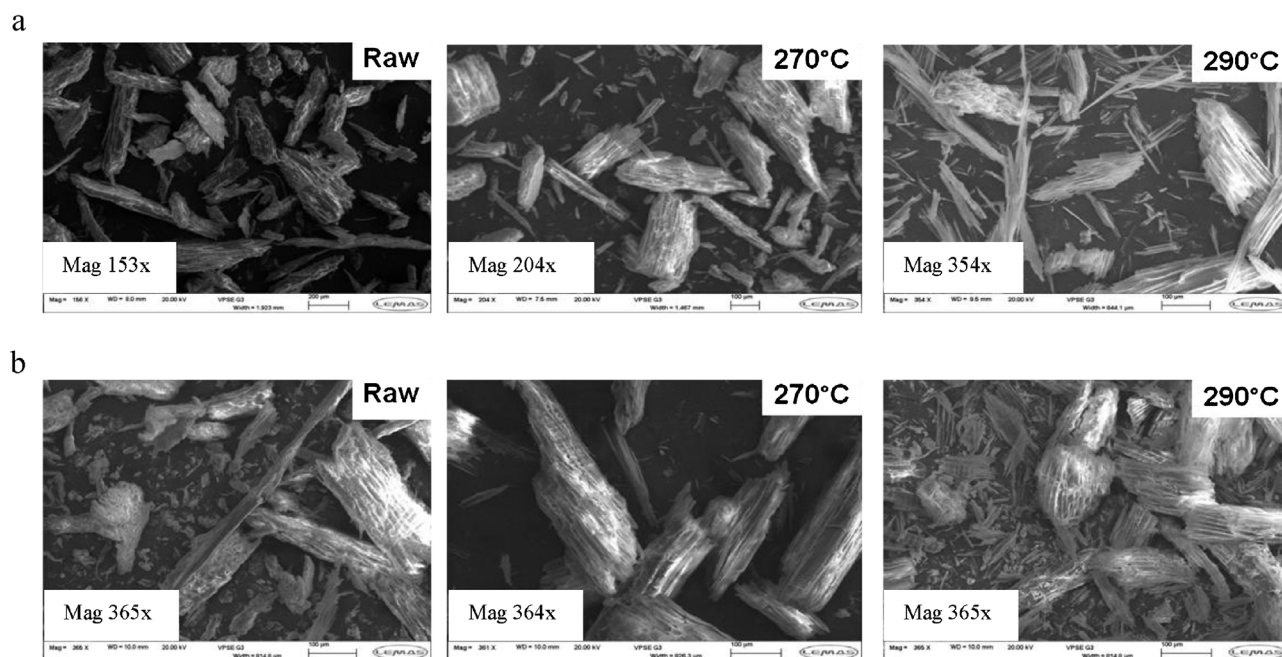


Fig. 9. SEM images of raw and torrefied (a) willow and (b) eucalyptus.

to the aromatic C–O stretching of methoxyl and phenyl propane units, and those at 1516 cm^{-1} and 1508 cm^{-1} could be due to the C=C aromatic ring vibrations [19]. These bands were present in the spectra of willow and eucalyptus A and B, but reduced in intensity in the spectra of the samples that received treatment C.

3.4.2. XPS measurements

The XPS technique has been used to investigate the chemical transformations that have taken place on the surface of carbon fibres (e.g. [34]), and more recently also of wood samples that have been heat-treated [35]. For this purpose, the C 1s signal is usually deconvoluted into four components that correspond to four types of carbon atoms bonded to either other elements or functional groups, as follows [35,36]: the signal for C_1 found at binding energy (BE) of 284.6 eV , has been attributed in the literature to carbon atoms bonded with carbon or hydrogen atoms only; the signal for C_2 carbon is typically found at slightly higher BE compared to C_1 ($\Delta\text{BE} = +1.5 \pm 0.2\text{ eV}$) and corresponds to a carbon atom bonded with one oxygen atom or ether/hydroxyl groups; the signal for C_3 carbon correspond to carbon atoms bonded to a carbonyl or two non-carbonyl oxygen atoms ($\Delta\text{BE} = +2.8 \pm 0.2\text{ eV}$); a C_4 carbon has been linked to carbon atoms bonded to a carbonyl and a non-carbonyl oxygen atom or carboxylic functionalities ($\Delta\text{BE} = +3.75 \pm 0.2\text{ eV}$) [35,36]. In contrast, data for the BE of the O 1s

signal are scarce, and the assignment of the oxygenated functional groups are still a matter of debate. However the O_1 peak at BE of $531.4\text{--}532.3\text{ eV}$ has been tentatively assigned to carbonyl groups, while the signal for C–O–R groups are expected at $533.0\text{--}534.0\text{ eV}$ [36]. Please note that the signal for moisture in wood is also expected to fall within the BE range for C–O– functionalities, at $533.0\text{--}533.5\text{ eV}$ [36].

The survey XPS spectra of the raw and torrefied fuels (not shown) indicate the presence of carbon, oxygen and a small proportion of nitrogen. High resolution scans of the XPS spectra of C 1s and O 1s levels for the analyses of raw and torrefied eucalyptus samples are shown with the deconvolutions of their peak envelopes in Fig. 11(a)–(d). The deconvolution of the XPS spectra of the C 1s signal of the raw eucalyptus, shown in Fig. 11(a), results in a large peak (at BE 284.6 eV) due to both carbon–carbon bonds and carbon–hydrogen bonds (C_1 type), which accounts for approximately 90% of the XPS signal. Also, a smaller peak (10%) can be found at BE of 287.5 eV , that has been tentatively attributed in the literature to ether/hydroxyl groups (C_2 type) groups. In contrast, the C1s spectrum of the torrefied eucalyptus A sample in Fig. 11(b) shows the disappearance of the ether/hydroxyl groups and a noticeable decrease of the C_1 carbon – from 90% to 47%, upon torrefaction. Additionally, the presence of carbonyl groups (C_3), are also detected, which were absent from the raw sample. Fig. 11(c) shows the O 1s spectrum of raw eucalyptus, where a peak for oxygen can be observed at BE of 533.1 eV , which could be attributed to ether groups (C–O–C), hydroxyl groups (C–OH) and possibly moisture [36]. In the case of the torrefied sample A (Fig. 11(d)), the O 1s spectrum shows two peaks, where in addition to the large peak assigned to C–O–C or C–OH groups (533.3 eV), there is also a peak at 531.5 eV , which could be due to the formation of carbonyl groups. The results of the XPS data agree with the observations from the FTIR spectroscopy investigations, which show that the heat treatment results in loss of OH groups and formation of C=O groups consistent with dehydration reactions and cross-linking. The result is a solid with a lower capability to hydrogen bond with water, and hence more hydrophobic.

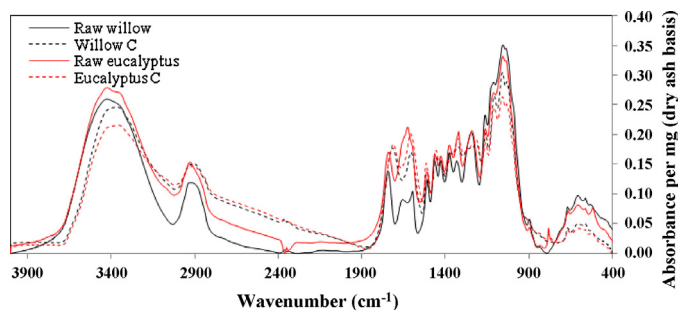


Fig. 10. FTIR spectra of raw and torrefied willow and eucalyptus.

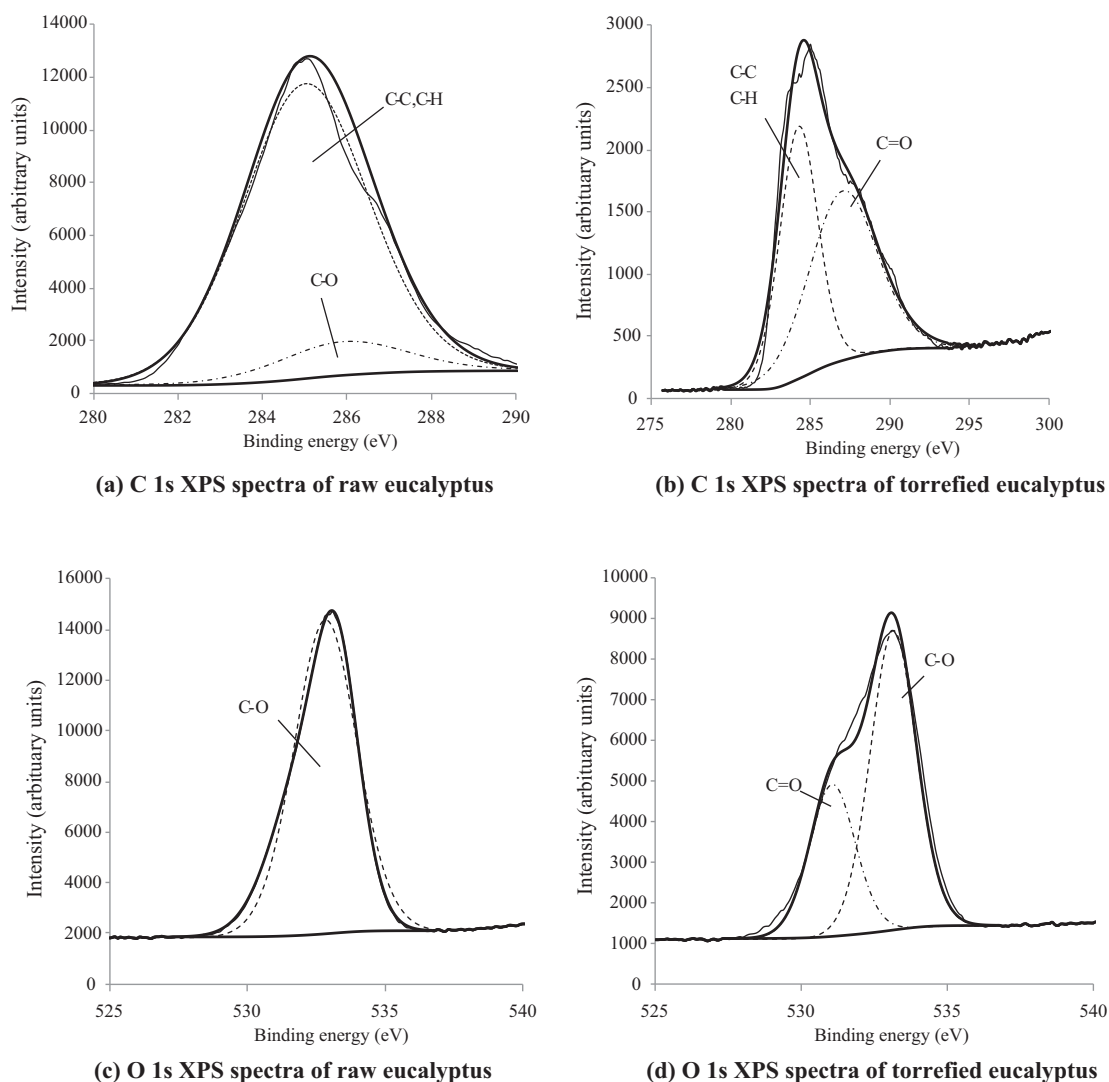


Fig. 11. XPS spectra of untreated eucalyptus and torrefied eucalyptus sample A, where (a) and (b) are the C 1s and O 1s XPS spectra of raw eucalyptus; (c) and (d) are the C 1s and O 1s XPS spectra of torrefied eucalyptus.

4. Conclusions

The physical and chemical characteristics of some torrefied woods have been investigated. Willow, eucalyptus, a mixture of hardwoods (oak and birch), and a mixture of softwoods (pine, spruce and larch) were torrefied at two temperatures (270 °C and 290 °C) and two residence times (30 and 60 min). Particular emphasis was given to the determination of coal-like grindability behaviour and to any changes in their morphological structure, as observed by microscopic and spectrometric methods. Overall, eucalyptus was observed to experience the greatest mass loss under these conditions, and although the resultant solid had the highest HHV of those studied, it nevertheless had the lowest energy yield. The next reactive fuel was the mixture of hardwoods, followed by willow, and finally the mixture of softwoods. An optimum operating condition to produce a high energy content is crucial. In this study, treatment at 270 °C with a residence time of 30 min resulted in a fuel with a mass yield of ~70% of and an energy content ~80–90%. Investigations of the torrefied solid indicate that the decrease in the O/C and H/C ratios upon torrefaction is accompanied by loss of –OH groups and an increase in C=O groups relative to C–O groups. The result is a more hydrophobic solid, since its hydrogen-bonding capacity is decreased. In addition, the solid becomes easier

to grind to small particle size, as measured by an equivalent Hard-grove Index test. For these conditions no obvious change in porosity or surface area were observed, at least with the techniques used. The energy yield of the torrefied solid appeared to vary monotonically with mass yield, but other properties did not. Rather there was a sudden change in properties such as grindability and hydrophobicity after a certain mass yield, and the point at which this abrupt change happens differed for the different samples.

Acknowledgements

The authors are grateful to the Energy Programme (Grant EP/H048839/1) for financial support. The Energy Programme is a Research Councils UK cross council initiative led by EPSRC and contributed to by ESRC, NERC, BBSRC and STFC. RHHI would also like to thank Brunei Government Scholarship for the support.

References

- [1] H. McKay, Environmental, economic, social and political drivers for increasing use of woodfuel as a renewable resource in Britain, *Biomass and Bioenergy* 20 (4) (2006) 308–315.
- [2] Brussels Commission of the European communities (CEC), Proposal for a directive of the European parliament and of the council on the promotion of the use of energy from renewable sources. [WWW]. Available from

- <http://ec.europa.eu/energy/climate_actions/doc/2008_res_directive_en.pdf>, 2008 (accessed 06.05.11).
- [3] Department of Energy and Climate Change (DECC), The UK Renewable Energy Strategy. [WWW]. Available from <http://www.decc.gov.uk/en/content/cms/meeting_energy/bioenergy/strategy/strategy.aspx#>, 2009 (accessed 08.10.12).
 - [4] W.-H. Chen, H.-C. Hsu, K.-M. Lu, W.-J. Lee, T.-C. Lin, Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass, *Energy* 36 (5) (2011) 3012–3021.
 - [5] Drax, Biomass: The Fourth Energy Source. [WWW]. Available from <<http://www.draxpower.com/biomass/>>, 2011 (accessed 11.01.12).
 - [6] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresource Technology* 83 (1) (2002) 37–46.
 - [7] E.S. Lipinsky, J.R. Arcate, T.B. Reed, Enhanced wood fuels via torrefaction, *Abstracts of Papers American Chemical Society* 223 (1–2) (2002) 171, Fuel.
 - [8] M.N. Nimlos, E. Brooking, M.J. Looker, R.J. Evans, Biomass torrefaction studies with a molecular beam mass spectrometer, *Abstracts of Papers of the American Chemical Society* 48 (2) (2003) 44, Fuel.
 - [9] B. Arias, C. Pevida, J. Ferosa, M.G. Plaza, F. Rubiera, J.J. Pis, Influence of torrefaction on the grindability and reactivity of woody biomass, *Fuel Processing Technology* 89 (2) (2008) 169–175.
 - [10] P.C.A. Bergman, J.H.A. Kiel, Torrefaction for biomass upgrading, in: 14th European Biomass Conference & Exhibition, Paris, France, 2005.
 - [11] S. Mani, L.G. Tabil, S. Sokhansanj, Grinding performance and physical properties of wheat and barley straws, corn starch and switchgrass, *Biomass and Bioenergy* 27 (4) (2004) 339–352.
 - [12] P.C.A. Bergman, Combined Torrefaction and Pelletisation: The TOP Process, Petten, The Netherlands, 2005.
 - [13] T.G. Bridgeman, J.M. Jones, I. Shield, P.T. Williams, Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties, *Fuel* 87 (6) (2008) 844–856.
 - [14] T.G. Bridgeman, J.M. Jones, A. Williams, D.J. Waldron, An investigation of the grindability of two torrefied energy crops, *Fuel* 89 (12) (2010) 3911–3918.
 - [15] M. Phanphanich, S. Mani, Impact of torrefaction on the grindability and fuel characteristics of forest biomass, *Bioresource Technology* 102 (2) (2011) 1246–1253.
 - [16] T.O. Rodrigues, P.L.A. Rousset, Effects of torrefaction on energy properties of *Eucalyptus grandis* wood, *Cerne* 15 (4) (2009) 446–452.
 - [17] M.J. Prins, K.J. Ptasinski, J.J.G. Janssen, Torrefaction of wood. Part 2. Analysis of products, *Journal of Analytical and Applied Pyrolysis* 77 (1) (2006) 35–40.
 - [18] D. Medic, M. Darr, A. Shah, B. Potter, J. Zimmerman, Effects of torrefaction process parameters on biomass feedstock upgrading, *Fuel* 91 (1) (2012) 147–154.
 - [19] M.J.C. Van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: a review, *Biomass and Bioenergy* 35 (9) (2011) 3748–3762.
 - [20] T. Melkior, S. Jacob, G. Gerbaud, S. Hediger, L.L. Pape, L. Bonnefois, M. Bardet, NMR analysis of the transformation of wood constituents by torrefaction, *Fuel* 92 (1) (2012) 271–280.
 - [21] R. Pentananunt, A.N.M. Mizanur Rahman, S.C. Bhattacharya, Upgrading of biomass by means of torrefaction, *Energy* 15 (12) (1990) 1175–1179.
 - [22] A. Pimchui, A. Dutta, P. Basu, Torrefaction of agriculture residue to enhance combustible properties, *Energy and Fuels* 24 (2010) 4638–4645.
 - [23] P. Rousset, F. Davrieux, L. Macedo, P. Perre, Characterisation of the torrefaction of beech wood using NIRS: combined effects of temperature and duration, *Biomass and Bioenergy* 35 (3) (2011) 1219–1226.
 - [24] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel* 86 (12–13) (2007) 1781–1788.
 - [25] DD CENT/TS 14774-2:2004, Solid biofuels. Method for the determination of moisture content – oven dry method. Part 2. Total moisture content – simplified method, 2004, British Standards, p. 6.
 - [26] DD CENT/TS 14775:2004, Solid Biofuels. Method for the determination of ash content, British Standards, 2004, p. 12.
 - [27] DD CENT/TS 15148:2005, Solid biofuels. Method for the determination of volatile matter, British Standards, 2005, p. 9.
 - [28] A. Friedl, E. Padouvas, H. Rotter, K. Varmuza, Prediction of heating values of biomass fuel from elemental composition, *Analytica Chimica Acta* 544 (1–2) (2005) 191–198.
 - [29] N.R. Joshi, Relative grindability of bituminous coals on volume basis, *Fuel* 58 (6) (1979) 477–478.
 - [30] F. Agus, P.L. Waters, Determination of the grindability of coal, shale and other minerals by a modified Hardgrove machine method, *Fuel* 50 (4) (1971) 405–431.
 - [31] O. Osazuwa-Peters, A.E. Zanne, Wood density protocol. [WWW]. Available from <http://prometheuswiki.publish.csiro.au/tiki-index.php?page=Wood+density+protocol>, 2011 (accessed 14.11.11).
 - [32] C. Morterra, M.J.D. Low, IR studies of carbons. II. The vacuum pyrolysis of cellulose, *Carbon* 21 (3) (1983) 283–288.
 - [33] J. Zawadzki, Infrared-spectroscopy in surface-chemistry of carbons, *Chemistry and Physics of Carbon* 21 (1989) 147–380.
 - [34] J. Ahrenfeldt, J.K. Holm, A.R. Sanadi, S. Barsberg, T. Thomson, W. Stelte, U.B. Henriksen, Changes of chemical and mechanical behavior of torrefied wheat straw, *Biomass and Bioenergy* 40 (2012) 63–70.
 - [35] R.H. Bradley, X. Ling, I. Sutherland, An investigation of carbon fibre surface chemistry and reactivity based on XPS and surface free energy, *Carbon* 31 (7) (1993) 1115–1120.
 - [36] G.N. Inari, M. Petrissans, J. Lambert, J.J. Ehrhardt, P. Gerardin, XPS characterisation of wood chemical composition after heat-treatment, *Surface and Interface Analysis* 38 (10) (2006) 1336–1342.